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Biodiesel production in Brazil and alternative biomass feedstocks

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ABSTRACT

Renewable biofuels are increasingly important in the Brazilian energy matrix. In 2010, the country became the second world producer of biodiesel with a production of 2.4 million of m^3 in that year, only behind Germany. In 2011, both the United States and Argentina increased production and now Brazil is the fourth world producer of biodiesel. The Brazilian biodiesel production federal program has been designed so that small family farmers, as well as large agribusiness operations, are encouraged to produce vegetable oil crops for biodiesel production. Brazil is the second largest world producer of soybeans, currently the main feedstock used for biodiesel production in the country. Due to the increasing demand for biodiesel and low oil productivity from soybean, Brazil is searching for alternative oilseed crops from which biodiesel can be produced. In this review, the current scenario for biodiesel production in Brazil is discussed, as well as vegetable oil crops that are being considered as potential biodiesel feedstocks in addition to soybeans. Brazil's biodiesel industry is currently operating only at 47% of its capacity. Therefore, it is expected that biodiesel production in Brazil will further increase. Due to the size of the country's bioethanol and biodiesel industries, Brazil can already be considered one of the world powers in sustainable biofuel production, an strategic area of the world's emerging bio-based economy.

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1. Introduction

World population growth is increasing the use of petroleum-derived energy resulting in high emissions of pollutants into the atmosphere. Fortunately, concern about the environment is growing and the scientific community is being challenged to improve existing renewable alternatives to petroleum-derived fuels and to create new ones. Renewable fuels will likely be an important product in bio-based economies.

Biodiesel is a fuel produced from vegetable oils, animal fats or waste vegetable oils and has been widely studied. Chemically, biodiesel is a mono ester alkali that can substitute oil diesel (petrodiesel). The degree in which this substitution will happen will depend on how economically competitive biodiesel is. For this it will need to be produced from renewable and abundant feedstocks, the largest component to the price of biodiesel. In 2010, Brazil became the second largest producer of biodiesel with a production of 2.4 million m^3, remaining behind Germany, the largest world biodiesel producer for 2010 with a production of 2.8 million m^3 [1]. In 2011, despite Brazil's increase in biodiesel production to 2.6 million of m^3 [2], it was surpassed by the United States which produced 3.7 million of m^3 [3] and Argentina which produced 2.7 million of m^3 of biodiesel [4]. Germany maintained production at 2.8 million m^3 [5] (Fig. 1). Brazil's ranking among the top world producers is largely a result of investments made in biodiesel research and production due to a governmental program.

Renewable energy sources are vitally important to Brazil's energy matrix. Sugarcane production for energy purposes (i.e., bioethanol) has a long-standing tradition in Brazilian agriculture. Brazil is currently not only a large producer of soybeans but also an important producer and consumer of biodiesel. Brazil's proven competitiveness in agribusiness and its understanding that the use of biofuels need to be expanded put the country in a key position in the biofuel market. However, the demand for biodiesel is increasing due to governmental policies and alternatives to soybean as a source for biodiesel should be encouraged, particularly crops with higher oil productivity. Other than soybeans, there are several oil crops that are candidate feedstocks for biodiesel production in Brazil. After a brief overview of the history of biodiesel in Brazil and biodiesel production, this review discusses the Brazilian federal program PNPB and candidate crops that may be used to produce biodiesel in Brazil in addition to soybeans. In this review, data from Brazilian government agencies that are not easily accessible to non-Portuguese speakers are presented. The current status, some challenges and future prospects for the biodiesel industry in Brazil are considered. The Brazilian experience should be of interest both to countries that are current competitors (i.e., large biodiesel producers), as well as to countries that are starting to look for business opportunities in this sector, particularly countries with similar tropical climate.

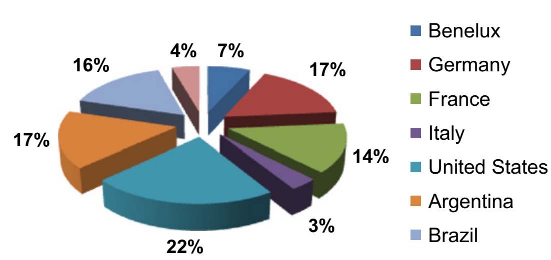

Fig. 1. World biodiesel production in 2011.
Source: Data from OECD [3].

2. Biodiesel production and early beginnings in Brazil

Natural oil has a viscosity 10 to 17 times higher than petrodiesel, which can cause damage to engines. To reduce viscosity, it is necessary for crude vegetable oil to be converted into biodiesel through a transesterification or esterification process [6]. For the biodiesel production process, vegetable oils can be extracted with solvent or mechanically by pressing the fruit or seed, depending on the plant species, which is followed by purification and a refining process [7].

In the transesterification process, reaction occurs between the triglyceride (oil) and an alcohol forming a methyl or ethyl-ester (i.e., biodiesel) as the main product and glycerin (i.e., glycerol) as a byproduct. To increase efficiency and reduce reaction time, a catalyst is used. Different catalysts such as acids, bases or enzymes can be used. Transesterification can occur with acid or base catalysts which can be homogeneous or heterogeneous [6]. While homogeneous catalysts function in the same phase as the reactants, heterogeneous catalysts act in a different phase than the reactants. Sodium hydroxide (NaOH) is widely used as a homogeneous base (i.e., alkaline) catalyst in transesterification for its efficiency and low price, as well as availability in the market [8].

Different types of alcohols can be used in the transesterification process including ethanol, methanol, propanol, butanol, and amyl-alcohol. Currently, the methanol route to biodiesel production is most commonly used in Brazil and in the world as this reaction has higher efficiency, occurs in a shorter time and lower temperature (60 °C) compared to other alcohols [9]. However, as methanol is obtained from fossil source (i.e., from methane) and it is toxic, ideally it should be substituted by alternative alcohols [8]. According to Freedman et al. [9], the transesterification reaction of soybean oil using methanol, ethanol and butane and 1% of sulfuric acid, achieved conversion between 96 and 98%, regardless of the alcohol used. As ethanol can mix better with oil than others alcohols, the excess of alcohol used to force the stoichiometry can be a problem later when the ester formed needs to be separated from ethanol. Because of the large production of ethanol in Brazil, it would be more advantageous to use ethanol to make biodiesel than methanol. Brazil is investing in research to improve this technology [8].

Because oil properties' are different for each oil crop species (for an extensive review on this subject see [10]), a particular biodiesel conversion process may be more suitable for each oil type. For example, more basic catalyst needs to be added to an acidic oil to neutralize the free fatty acids (FFA) (i.e., long-chain carboxylic acid) or it could be necessary to use an acid catalyst instead [11]. Both the alcohol and the oil used in this reaction need to be anhydrous, as the presence of water in the reaction can lead to the production of soap from the FFA. This undesirable byproduct decreases ester production efficiency and complicates the purification of glycerol.

A second route to produce biodiesel is through esterification. In an esterification reaction, a FFA reacts with a low molecular weight alcohol such as methanol or ethanol producing ester (i.e., biodiesel) and water. This process can be used when the oil is acidic (i.e., acidity > 5) such as FFA-rich oil resultant from the refining of vegetable oils, animal fats obtained from the slaughterhouse, as well as oils obtained from sewage [7]. For FFA-rich oils, the use of basic catalysts is not recommended, once it can combine with the FFA to form soap. The use of homogeneous acid catalysts for esterification can be used instead. However, it is difficult to remove the residual catalyst from the esterified product [7].

In both transesterification and esterification processes, another option instead of using chemical catalysts is to rely on

enzymes (i.e., lipases) for catalysis. The yield of biodiesel production using enzymatic catalysts is high, especially when using refined oils instead of crude oils. Crude oils contain phopholipids that can affect the interaction between enzyme and substrate [12]. Lipase catalysts are more active on insoluble substrates and on triglycerides of long chain fatty acids. For short chain triglycerides (i.e., less than 6 carbons), esterase enzymes can be used as catalysts. The use of enzyme catalysts is more advantageous than base or acid catalysts because they can be recovered and reused or can be used in an immobilized form. Also, the process occurs at low temperatures (e.g., 40 °C) in comparison to chemically catalyzed processes. However, one of its drawbacks is that commercial lipases are expensive, a problem for large-scale industrial operations.

In Brazil, the earliest reference to the use of vegetable oils as fuel occured in 1920. At that time, many universities began to invest in research using in natura oil blended to petrodiesel as a fuel. The research centers in Brazil that participated in these studies were the National Institute of Technology, the Oil Institute of Ministry of Agriculture and the Industrial Technology Institute of the state of Minas Gerais [13].

In 1973, a petroleum crisis impacted global economy and research for renewable fuels was again intensified. Back then, Brazil imported 80% of the petroleum needed. In the same decade, the National Institute of Technology and the Institute for Technological Research began to study biodiesel made from palm oil ('dende' in Portuguese), calling it dendiesel [13]. In the following years, with the end of the petroleum crisis, petrodiesel became cheaper and research on biodiesel was no longer a priority.

The use of biodiesel in Brazil became more common in the 80s when a number of governmental programs were launched. In 1980, the National Program for Vegetable Oil Production for Energy Purposes (Proóleo) was launched following resolution no. 7 of the National Council of Energy. This program aimed to replace 30% of petrodiesel by vegetable oil, encourage researchers to increase the production of vegetable oils in different regions of the country and to try to replace the petrodiesel by biodiesel [13]. Due to the drop in petrodiesel prices in 1985, this program was abandoned. Still in the 80s, the Industrial Technology Secretary launched the National Energy Program from Vegetable Oils (OVEG) that aimed to test vegetable oils in diesel engines. Different tests with pure biodiesel and with B30 biodiesel (i.e., 70% petrodiesel and 30% biodiesel blend) were performed, but due to the high cost of production, commercial scale use of biodiesel was not feasible at the time [8].

In 2002, the Ministry of Science and Technology launched the program Probiodiesel. This program aimed to reduce biodiesel imports because of high prices, to expand the market for vegetable oils and to decrease emission of greenhouse gases, as Brazil is a signatory country for the Kyoto Protocol. In 2003, the Ministry of Mines and Energy launched the Green Fuel Program which also intended to create more farm jobs [8]. In the same year, came decree no. 02/07/2003 and a commission at the ministry level was formed to lay the foundation for the National Program for Use and Production of Biodiesel (PNPB). PNPB was created in December 2004 and, as will be discussed in detail in the next section, it is currently the most important Brazilian government biodiesel public policy program. In 2004, the state of Pará Biodiesel Program was created, contributing to its current status as the largest producer of palm oil in Brazil [14]. In 2005, the first year of the PNPB program, Brazil produced 736 m^3 of biodiesel increasing production by more than 500 fold to 399,243 m^3 in 2007; with the state of Goiás being the largest producer of biodiesel, mainly from soybeans [11]. In 2008, the world faced another petroleum crisis and prices became abusive. Brazil took this as a warning and started to invest again in research on renewable fuels.

3. The Brazilian National Program for biodiesel production and use (PNPB)

According to law no. 11.097/2005, as of January 2008, the use of 2% biodiesel blended with petrodiesel (B2) is mandatory in Brazil and increasing amounts of biodiesel blended with petrodiesel will be required with time. Currently Brazil is using B5 diesel, which became mandatory before the scheduled date. Therefore, the demand for biodiesel tends to increase and the PNPB came as an important instrument of public policy in the sector.

PNPB defines biodiesel as a fuel derived from biomass that can be used in internal combustion engines with compression ignition. As such, biodiesel has emerged to replace petrodiesel, partially or completely. PNPB aims to reduce Brazil's dependence on imports of petrodiesel and to seek new sources of renewable energy. PNPB was also designed to encourage small farmers (family farms) to produce feedstock for biodiesel production and become an important part of this biofuel production chain. This is accomplished in part through the Social Seal, a certificate provided by the Ministry of Agrarian Development (MDA) to biodiesel producers that buy oil from family farmers at specific percentages from each geographical region of Brazil. In turn, biodiesel producers with the Social Seal get fiscal benefits from the Federal government [15]. For example, a 68% reduction in federal taxes (i.e.; PIS/PASEP and COFINS taxes) is granted to biodiesel producers that buy oil seeds from family farms and up to 100% tax reduction can be obtained if the acquisition of oil is from oil palm family farmers from the North or Northeast regions or castor bean family farmers from the semiarid region of Brazil. Biodiesel producers with a Social Seal also benefit from credit lines with favorable rates from banks such as BNDES, BASA, BNB and Banco do Brasil. Mills that have the seal can also participate in auctions buying and selling the biodiesel [16]. Family farmers also get special credit lines [15].

Another interesting feature of PNPB is that biodiesel producers and family farmers are bound by a contract establishing the price the family farmer will get for the oil as well as the date the oil has to be delivered to the biodiesel producer. In addition, biodiesel producers supply technical assistance to family farmers [15]. In this way, PNPB has been able to encourage the structuring of the sector with small farmers and the industry working in concert. In 2010, 20% of biodiesel production came from family farming; with 103,000 farming families participating in the biodiesel production chain [17]. In 2011, the number of farming families increased to 105,000 [18]. Furthermore, PNPB seeks to diversify the oil crops from which biodiesel is produced, as well as the region of the country where they are planted. In practice, it attempts to give an opportunity to feedstocks other than soybeans produced by large agribusiness operations [15]. Crop and region of origin diversification allows for a more stable supply of oil for biodiesel production throughout the year.

Large areas available for agriculture and governmental incentives can lead Brazil to become an even more important biodiesel producer. However, the ultimate challenge for the future is to make biodiesel that is cost competitive with petrodiesel. Thus, technologies are being developed to improve biodiesel production in Brazil.

4. Candidate crops for producing biodiesel in Brazil

In 2011, Brazil produced 2.6 million of m^3 of biodiesel, with the Center-west region of the country being the main producer (Fig. 2a) [19,20]. Brazil has increased its biodiesel production over the years (Fig. 2b), however, its mills are not producing at

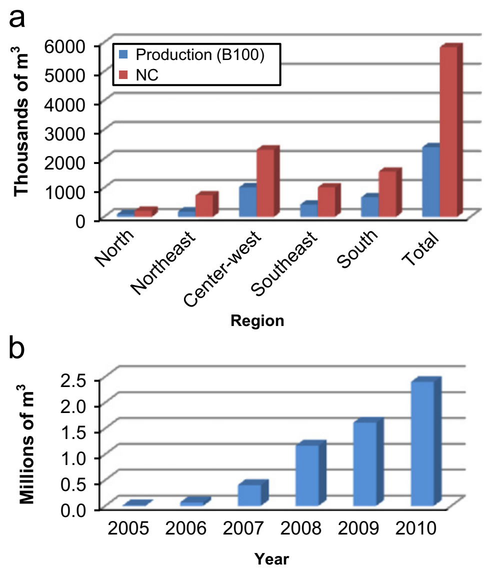

Fig. 2. Biodiesel production in Brazil and nominal capacity (NC) for each region. Nominal capacity refers to the amount of biodiesel that can be produced if all mills were producing at full capacity.
Source: Data from ANP [84].

maximum capacity (i.e., nominal capacity) (Fig. 2a). Because of its large areas available for agriculture, Brazil can increase the planted area with biodiesel feedstocks without interfering with pasture areas or areas used for feed crops [17]. Given the demand for biodiesel and the possibility of increasing production, it is likely that production of biodiesel will continue to increase.

Soybeans (*Glycine max*), which will be discussed in detail below, have traditionally been the feedstock used for biodiesel production in Brazil. Its production chain is well organized and this has been one of Brazil's most successful large scale agribusiness operations. Brazil's research efforts to develop agricultural technology for the tropics in the 60s, mainly by the Brazilian Agricultural Research Corporation (Embrapa), are directly responsible for the soybean industry of today. Soybean varieties adapted to Brazilian conditions of warmer temperatures and longer growing season than temperate regions were developed. This allowed growing soybeans in the Cerrado of Brazil, a type of savannah, located in the Center-west region of the country (i.e., over 1000 km from the Amazon forest). Originally, highly productive agriculture was not thought possible in Cerrado, mainly because of poor quality soils, with low pH and high levels of aluminum. Research led to effective measures to correct the soil, crop management practices were optimized, and these coupled with mechanization allowed for low operating costs and high yields.

Because biodiesel is a product for the energy sector, oil to produce biodiesel needs to be inexpensive and available in large amounts. Brazil is a large country with many regional differences in climate and soil. To increase the availability of oil and better use its regional resources, alternative vegetable oil crops to soybeans are being considered. These include oil palm, physic nut, coconut, babassu, sunflower, rapeseed, castor bean, peanut, and cotton (Table 1). Most of these have long been cultivated in Brazil for purposes unrelated to biodiesel and were mentioned in the Brazilian National Plan for Agroenergy [21]. There are also lesser known species being considered for biodiesel production which include the palm trees tucumã (*Astrocaryum aculeatum*), inajá (*Attalea maripa*), macaw palm (*Acrocomia aculeata*), buriti (*Mauritia flexuosa*) and licuri (*Syagrus coronata*).

Table 1
Comparison of oil crops grown in Brazil.

Crop	Oil content (%)	Plant cycle	Oil yield (kg/ha)	References
Oil palm (fruit)	22	Perennial	2000–8000	[24,27]
Physic nut (kernel)	38	Perennial	1200–1500	[34,35,82]
Coconut (copra)	58–65	Perennial	1481	[43,44]
Babassu (kernel)	60	Perennial	120	[51]
Castor bean (seed)	39.6–59.5	Annual	470–810*	[34,60,83]
Peanut (grain)	40–60	Annual	788	[24,64]
Sunflower (seed)	40–47	Annual	774	[24]
Soybean (grain)	18–21	Annual	560	[24]
Rapeseed	34–40	Annual	570	[34]
Cotton (seed)	18–20	Annual	361	[24]

* 810 kg/ha was calculated considering a productivity of 1.8 t/ha and an industrial oil yield of 45% [83].

Comparing such different plant species on their potential for oil production for biodiesel is difficult. Different parts of the fruit can be used for oil extraction in different species. Coconut oil is extracted from the endosperm, in oil palm the mesocarp and seed of the fruit are used, while in babassu, peanut, rapessed, castor bean, sunflower, physic nut, soybean and cotton the oil is extracted from seeds. Further, the oil content of the mesocarp/seed/whole fruit varies between species (Table 1). Anatomical differences related to location of the oil in the fruit, as well as the oil content may be important factors in determining how difficult it is to extract the oil. Babassu has 60% kernel oil content but access to the kernel may be a problem. Some oil crops are perennial, while others are annual (e.g., peanut and sunflower can be planted two times a year); some produce year round, while others produce only during a certain time of the year (Table 1). For some oil crops, cultivation practices are well established and mechanized harvesting is common (e.g., cotton, sunflower, soybean, peanut and rapeseed); for others, harvesting is manual (e.g., coconut, palm tree and babassu) [22,23]. Keeping in mind the differences between oil crops, it is still useful to compare them on their potential for producing oil for the biodiesel industry. It is clear that although soybeans have traditionally been grown in large scale in Brazil, they have low seed oil content (18–21%) and low yield at approximately 560 kg of oil/ha [24], compared to other plants (Table 1). Oil yield data indicate oil palm and physic nut, which can produce as much as 8000 and 1500 kg of oil/ha, respectively, as the most advantageous biodiesel feedstocks. The main characteristics and potential for biodiesel production of the plant species mentioned above will be discussed in the following sections.

4.1. *Oil palm*

Oil palm (*Elaeis guineensis* Jacq.) is a perennial plant of Arecaceae family (Fig. 3) that originated in West Africa. It is currently an important feedstock for biodiesel production in Malaysia and Indonesia. In Brazil, oil palm is mainly produced in the north of Bahia state and the state of Pará (Fig. 4) [25]. Palm oil can be extracted from two parts of the fruit (Fig. 3): the pulp (i.e., mesocarp) which contains 20–22% of oil and the seed (i.e., palm kernel oil) which has 38–55% of oil content [26]. In Brazil, a 22% oil content for the whole fruit has been reported (Table 1) [24]. Kernel and pulp oil are mostly used in culinary applications as in margarine, ice creams and frying oils. As for non-culinary uses, both oils can be used to make soap, detergent and cosmetics. Among the oil seed crops, the oil palm is the one with the highest oil productivity reaching 5 to 8 t of oil/ha (Table 1) [24,27], which is about 10 times more oil than soybeans (Table 1). The oil palm lives about 25 years [25] and begins to produce fruits at 3 years of

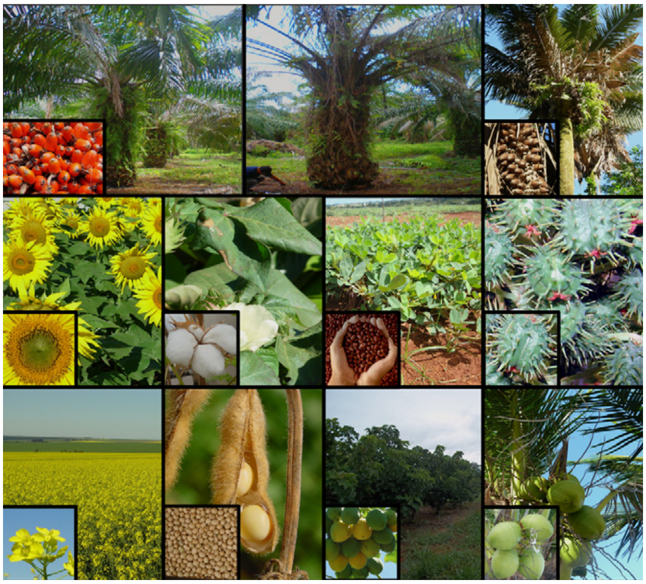

Fig. 3. Candidate oil crops to produce biodiesel. Healthy palm oil tree inset, palm oil tree fruits, palm oil tree in advanced stage of yellowing fatal disease, babassu inset. Babassu tree fruit. Sunflower inset, sunflower seeds, cotton plant inset, cotton flower, peanut plant inset. Peanut seeds, castor bean inset, castor bean fruits. Rapeseed, rapeseed flower, soybean pods, soybean seeds, jatropha inset. Jatropha seeds, coconut tree and inset, Coconut fruit.

Fig. 4. Candidate crops to produce biodiesel by region in Brazil. Soybean and sunflower are mainly produced in the South (blue) and Center-west (purple) regions. Rapeseed is produced in the South. Cotton is produced in South (Parana State) and Southeast region (orange). Coconut, peanut and physic nut are mainly planted in the Northeast region (green). Castor bean is produced in Northeast. Palm tree is mainly produced in the states of Bahia and Pará. Babassu is present in the Northeast and North regions (pink). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

age. Peak productivity occurs in the 8th year (25 t/ha), although the plant remains producing until the 17th year [25].

In 2010, Brazil was the 10th producer of palm oil [28]. Indonesia is the largest producer of oil palm with eight million hectares planted. Together, all other oil palm producing countries account only for a planted area of 2 million hectares. Brazil has an oil palm production of 1,292,713 t in 108,919 ha [29].

One major problem in using palm oil for biodiesel production is that it is acidic, requiring processing within 24–48 h after harvest to avoid a decrease in oil quality. Loss of oil quality is due to enzymatic deterioration, with hydrolysis of triacylglycerides and consequent increase of FFA, an undesirable product that in the presence of sodium hydroxide can form soap instead of biodiesel in the transesterification reaction [11].

Of all the vegetable oils, palm oil is the leading candidate for the production of biodiesel in Brazil in the future. However, Brazil still needs to become self-sufficient in its production, as today Brazil imports palm oil. Improvements on crop management need to be made. Fruit bunches are harvested manually, a time consuming and costly process. Furthermore, one major problem for growing oil palms in Brazil has been the occurrence of fatal yellowing (FY) (Fig. 3). FY appears sporadically in the field, the first symptoms being yellowing of leaflets on young leaves, a state that progresses to complete necrosis. Once the oil palm spear withers and dies, the plant stops producing fruits. FY has decimated over 5000 acres of oil palm in Brazil [30]. Both biotic and abiotic causes have been hypothesized and investigated without a conclusive answer. There are a number of ongoing breeding projects in Brazil to obtain oil palm plants resistant to FY. In 2010, EMBRAPA released the FY-resistant oil palm variety BRS Manipur, an interspecific hybrid between *E. guineensis*, the African oil palm, and *E. oleifera*, the American oil palm, locally known as caiaué. Although resistant to FY, the hybrid produces less oil than the African oil palm [31].

4.2. Physic nut

Physic nut (*Jatropha curcas* L.) is a perennial plant of the Euphorbiaceae family (Fig. 3) and its center of origin is most likely Mexico and Central America [32]. Harvesting occurs during 3 months of the year. Physic nut is grown in Brazil in the states of in Minas Gerais, Bahia, Goiás, Mato Grosso, Maranhão, Rio de Janeiro and Tocantins (Fig. 4) [33]. This crop is tolerant to water stress and can be planted in semiarid regions [32]. Regardless of the fact that Jatropha is a non-domesticated crop, it has been commercially produced in Brazil since 2004. However, lack of technical knowledge about this crop has led to low productivity [33]. Little is known about the pests and microorganisms that attack Jatropha or how to control them. There is no information about the ideal type of soil, declivity and altitude to cultivate Jatropha [33]. Despite these challenges, Brazilian farmers have shown interest in Jatropha as a crop for biodiesel production because of the high seed kernel oil content of approximately 38% (Table 1) [34]. The plant can give an oil yield of 1200 to 1500 kg/ha [35]. Brazil produced 116.03 t in 41,098.3 ha in 2011 [36].

The Jatropha seed (Fig. 3) is toxic; an advantage as its use for biodiesel production does not compete with possible uses as food. Seed toxicity has been attributed to a protein called curcin and phorbol esters. However, as discussed by King et al. [37], toxicity is most likely due to phorbol esters and not to curcin. Even after extracting the oil from the seeds, the cake (i.e., pomace) still contains approximately 11% of highly toxic oil [32]. Rumen microbes are not able to degrade phorbol esters, thus, the untreated cake cannot be used in feed even for ruminants which are less prone to toxicity than monogastric animals [38]. Research projects aiming to detoxify the protein-rich Jatropha cake are underway. A detoxified cake could be sold as animal feed, being further incentive for farmers to plant Jatropha.

Jatropha fruits do not ripen synchronously, thus increasing the costs of harvesting and making mechanization more challenging

[39]. Furthermore, oil extraction from fruits at different ripening stages has a negative impact on oil quality [39]. Studies of mechanized and semi-mechanized harvesting of Jatropha fruits are being made; and some of the methods are described on "The Jatropha Handbook". However, there is still no efficient mechanization method for harvesting Jatropha fruits [39].

Many of the current problems of Jatropha as a biodiesel feedstock crop (e.g., variable productivity, susceptibility to pathogens, lack of synchrony in fruit maturation) may be solved using a genetic approach. However, a study of 192 Brazilian accessions of *J. curcas* with RAPD primers and six selected microsatellite markers revealed low genetic diversity, a problem for plant breeding programs [40]. Interestingly, nontoxic genotypes of *J. curcas* low in phorbol esters have been found in Mexico and these can be identified with molecular markers.

Recently, the whole *J. curcas* genome (i.e., ca. 286 Mbp) has been sequenced. This will be useful not only for developing tools to genetically improve this crop, but also to increase the understanding of the basic biology of this species [41].

4.3. Coconut

Coconut (*Cocos nucifera*) is a perennial species of the Arecaceae family (Fig. 3) widely distributed in the tropics. The introduction of this palm tree in Brazil occurred before the colonization of Brazil by the Portuguese. Today coconut is found throughout the coast of Brazil, between the states of Rio Grande do Norte and Bahia (Fig. 4) [42]. The coconut tree takes 7 years to start producing, after which fruits can be harvested every 1.5 to 3 months [22]. There are two basic types of coconut tree: the tall variety Typica Nar. and the dwarf variety Nana Griff. Each of these varieties has certain advantages that can be combined in a hybrid variety. The tall and the hybrid varieties have high oil yields; the dwarf has a high production of coconut water. The main reason coconut became a candidate for biodiesel production is its high oil content. The desiccated coconut endosperm (i.e., also known as copra or coconut flesh) (Fig. 3) has 58–65% of oil content [43], and oil yield is between 1481 kg/ha [44]. In 2011, Brazil produced 1,8999,355 t of coconut in 261,824 ha and imported 264,934 kg [45]. Large investments are needed to increase coconut production if its oil is to be used in the biodiesel industry.

4.4. Babassu

Babassu (*Attalea speciosa*) is a perennial plant of the Arecaceae family. The taxonomy of species in the genus Attalea is still confusing [46]. Babassu is native to the southern part of the Amazon (Fig. 3) [47] and currently grows in the States of Maranhão Tocantins, Piauí and Pará (Fig. 4) [23]. The state of Maranhão accounts for 94% of the total production in Brazil [48]. The babassu palm takes approximately 12 years to start production and the first bunch takes nine months to mature [23]. In subsequence years, babassu can be harvested throughout the year [49]. There is no systematic cultivation of babassu in Brazil and current production comes from spontaneous babassu palm trees that occur in clusters (i.e., babassu forests). The Brazilian babassu production area occupies about 17 million ha, but this data is not exact [50] as the occurrence of babassu palm trees is sporadic. The babassu palm tree (Fig. 3) can be fully used. From its seed, oil to produce biodiesel is extracted, the pie is used as animal feed and the bark can be burned for energy [8]. The reason that this plant became a candidate to produce biodiesel is that the fruit endocarp has about 60% of oil and the plant produces approximately 120 kg of oil/ha [51]. The cost of oil extraction is high because it is manual. There are no commercial plantations of babassu palms in Brazil, and there is little knowledge about babassu palm crop management.

4.5. Sunflower

Sunflower (*Helianthus annuus*) is an annual crop of Asteraceae family and was introduced in Brazil by European immigrants. It is not one of the major crops in the country since it competes with soybeans and corn that are planted in the same period of the year. In 2011, the area used for sunflower cultivation was 66,400 ha with a total production of 83,100 t [52]. The central region of Brazil is the largest producer generating 64,000 t in 2010/2011; most of the production is destined for bird food, a few companies produce biodiesel from sunflower seed oil [52].

Sunflower seed oil presents high nutritional value and it can be extracted at room temperature without chemical products. Sunflower has a high oil yield at 774 kg/ha. In 2010, world sunflower oil production was 12,206,000 t. The major producers being Ukraine followed by Russia, the E.U. and Argentina [53]. In Brazil the percentage of biodiesel produced from sunflower oil is only 0.04%, comparable to that of castor oil [24].

4.6. Rapeseed

Rapeseed (*Brassica napus*) is a weed of the Brassicaceae family (formerly Cruciferae). Its origin is uncertain, but it is likely to be native from the Mediterranean area or Northern Europe. Rapeseed oil is commonly known as "Canola", however, this name stands for Canadian oil, low acid and was a trademark of the Canola Council of Canada. Native rapeseed was inedible and its oil used as machine lubricant. It contains erucic acid, which is toxic to humans in high concentrations, and glucosinolates, which gives the oil an unpleasant flavor. In the late 1970s, Canadian scientists used classic plant breeding methods to develop cultivars from *B. napus* and *B. rapa* (*campestris*) without the undesirable characteristics. Since 1986, the name canola was used as a general term to define rapeseed oil that contains less than 2% erucic acid, and less than 30 μmoles/g glucosinolates [54].

Oil content in rapeseed ranges from 34 to 40% [34]. It is the primary oilseed crop in Europe, and its oil production is mainly directed to industrial purposes, especially biodiesel [55]. In Brazil, rapeseed started being planted in 70s in the southern area of the country as a rotation crop for wheat. The cultivation of canola in Brazil has been in expansion since 2005, when Embrapa developed hybrid cultivars resistant to diseases caused by fungi [56]. The area of rapeseed production in 2010/2011 was 46,300 ha and the production was 69,700 t, with 94% of this production from the southern region of Brazil [52].

Rapeseed oil production in Brazil is mostly for the food market, the use for biodiesel is practically inexistent, but it is considered by the Brazilian government as an alternative to soybean. The Brazilian government is encouraging rapeseed crop expansion to other regions of the country. The introduction of canola in the Center-west region of Brazil has generated promising productivity results, and in 2010/2011 it accounted for 6% of Brazilian total production [56].

4.7. Castor bean

Castor bean (*Ricinus communis* L.) is an annual plant of the Euphorbiaceae family (Fig. 3) native to Africa [57] that is harvested during 3 months per year [49]. It was introduced in Brazil by the Portuguese during colonization. It is produced in the northeast of Brazil, mainly in the state of Bahia (Fig. 4) by family farmers [50]. Castor bean oil has wide application in the chemicals industry (e.g., it is used to produce paint, varnishes and lubricants) and cosmetic

industry (e.g., it is used to produce soap and shampoo). One of the reasons it has been considered for biodiesel production in Brazil, is that castor bean is a drought-tolerant plant, well adapted to semi-arid regions or places with long dry periods. In 2011, Brazil had 128,200 ha of castor bean planted area and a production of 24,800 t of seeds [58]. In 2005, family farmers were encouraged to plant castor bean, but lack of buyers made the price fall and producers lost interest. This situation was reversed after the company Petrobras Biofuels opened a pilot plant for producing biodiesel with castor bean oil in the city of Candeias in the state of Bahia, northeastern region of Brazil. The varieties of castor bean that are used commercially in Brazil are BRS188 and BRS149, developed by Embrapa Corporation and are ideal for altitudes between 300 and 1500 m and temperatures between 20 °C and 30 °C [59]. The castor bean seed (Fig. 3) has approximately 39.6–59.5% of oil [60], but the yield is only 470 of oil/ha (Table 1) [34]. Castor oil has unique chemical properties: high viscosity, physical and chemical stability and solubility in alcohol at low temperatures [61]. Castor bean oil is composed mainly (90%) by ricinoleic fatty acid that has a hydroxyl (OH) group largely responsible for the oil's chemical properties. Ricinoleic acid is unsaturated and has a low fusion point (−5 °C) [6]. These properties make it difficult to separate the glycerol from castor bean biodiesel in the final stage of the process [62]. Despite these difficulties, in 2009, Petrobras announced that it has established a biodiesel production process from castor oil [63].

4.8. Peanut

Peanut (*Arachis hypogaea*) is a perennial plant of the Leguminosae family native of South America (Fig. 3). Worldwide, peanut occupies the fourth place in importance of all oilseed crops [64]. However, the world production of peanut oil in 2006/2007 was of 4.85 million t, which corresponded only to a 4.9% of the total world oil production [65]. In Brazil, peanut crops are found mostly in the southeast, south, center-west, and northeast regions [24,66]. São Paulo state, in the southeast region of the country, which produces peanut in rotation with sugarcane, is the largest national producer, corresponding to 80% of Brazil's peanut production [24,67]. Brazilian peanut oil production was of 232,200 t in 2009/2010, which is less than the production of soybean oil (67,860,000 t) in the same year [24,65]. In 2010, the contribution of soybean oil to the production of biodiesel in Brazil was of more than 80%, with only about 0.1% of peanut oil [24].

Oil content in peanut ranges between 40 and 60% [24,64]. Interestingly, the first biodiesel ever produced was derived from peanut oil, by Rudolph Diesel, in early 1900s [11]. The oil yield for peanut is estimated to be 788 kg/ha [24]. Peanut presents a high nutritional value and it is an important food crop in Brazil; particularly in the northeastern part of the country [65]. Since peanut crops are sensitive to droughts, EMBRAPA has developed drought-tolerant varieties that are recommended for cultivation in the northeastern part of Brazil [24].

Costs for peanut production are low, since the process of harvesting is mechanized; however, this cost is increased by the need of disease control methods. In addition, this oilseed can be infected by fungi belonging to the genus *Aspergillus* that produce aflatoxins, a toxin that may cause liver damage and may be lethal to animals. EMBRAPA recommends several crop management procedures to control aflatoxins and developed peanut varieties that are more resistant to pests in general [68].

4.9. Soybean

Soybean (*Glycine max*) is a perennial crop of the Leguminosinae family (Fig. 3). Its seeds have approximately 18–21% oil content [24]. Today soybeans are cultivated as a monoculture in large agribusiness operations in part of the Center-west, Northeast and South regions of Brazil (Fig. 4) [69]. It is an annual crop with 3 months of harvesting [49]. In the recent past, soybean crops increase every year and 25,042 million ha were planted in 2011. In 2011, 66.4 millions of tons of soybeans were produced, making Brazil the second world producer of this crop [58]. The Brazilian industry uses 30.7 million t of soybean per year to produce 5.8 million t of edible oil and 23.5 millions of tons of protein bran. Brazil ranks third in the world as soybean oil exporter [17]. The high quality of Brazilian soybean seeds (Fig. 3) and its high protein content make it an excellent export product [70]. Brazil exports most of the grain to be used mainly as animal feed, with the oil being less economically valuable [17]. The increase in soybean production in Brazil is related to the increase in number of cattle, as soybean is the main ingredient in cattle feed in Brazil [17].

A major problem with soybeans as a crop used for biodiesel production is its low seed oil content (i.e., only 18%) if compared to others oil seeds. If alternative crops with higher oil yield do not become more important in the next few years, increasing demand for biodiesel production will require more soybean to be planted in Brazil. In this scenario, it is estimated that by 2020/2021, the planted area in Brazil dedicated to soybeans will have expanded to 30 million ha [71].

4.10. Cotton

Cotton (*Gossypium hirsutum latifolium* Hutch LR) is a herbaceous annual plant of the Malvaceae family (Fig. 3) that is harvested 3 months per year [49]. Its origin is not well defined, but the use of cotton fibers can be traced back centuries before Christ. In Brazil, the cotton-producing states are Mato Grosso, Bahia, São Paulo, Paraná and Mato Grosso do Sul [72] (Fig. 4). In 2011, 1.4 million ha of cotton were planted in Brazil and 3.2 million t of cotton seed were produced [72]. Cotton was chosen as a candidate for biodiesel production because of its low price. Today, cotton oil is the third feedstock for biodiesel production in Brazil, only behind soybean oil and beef tallow [20]. However, cotton seed has an oil content in the range of 18–20% [24] and oil yields are low at approximately 361 kg/ha [24], requiring large planted areas to obtain a small amount of oil. Cotton has well established agricultural management practices, usually involving a lot of chemicals as insects are attracted by flower buds [23] (Fig. 3). Excess pesticides may contaminate groundwater [23], which may be a problem in large plantations for biodiesel production. Another problem is that the pie that remains after cotton oil extraction cannot be used as animal feed because of the presence of toxic gossypol. Recently, using RNAi, Rathore et al. [73] reported silencing the gene for cadinene synthase to produce seeds with low levels of gossypol.

4.11. Exotic oil producing species found in Brazil

Many of the lesser known and more exotic oil producing plants being considered for biodiesel production are not domesticated. Thus, significant research efforts will be needed to make these plant species into economically viable alternatives to soybean in the future. Investment in germplasm collections and plant breeding programs will be needed, as well as the development of crop management practices. Despite these challenges, the five plant species described below have in common fruits with high oil content, and they may be used as feedstocks for biodiesel production in the future.

Tucumã (*Astrocaryum aculeatum* Meyer) is a palm tree native to the Northeast and Center-west of Brazil. It reaches 20 m, and produces 2 cm in diameter orange-colored ovoid fruits. The fruit pulp is sticky and fiber-rich. There are few studies about its

production system. Tucumã leaves can be used for its fibers and its fruits have culinary applications. The fruits present an oil content of approximately 47% and are rich in vitamin A [74]. The oil content in the mesocarp is 30%, while 40–50% oil is found in the endocarp [75]. The fruiting of the tucumã palm tree occurs throughout the year. There are no data about the production system of this palm tree. Studies show that tucumã seeds take more than 1000 days to germinate, but with proper handling this time can be reduced to 3 or 4 months [76].

Inajá (*Attalea maripa*), a palm tree also known as najá or coco-inajá, is found throughout the Amazon region, especially in the states of Pará and Maranhão. Maranhão is a state geographically in the Northeast region (Fig. 3) but it is a transition between the Amazon and Caatinga biomes. This palm tree reaches 20 m in height and is highly resistant to fire. The Inajá fruit is appreciated for its sweet flavor. The seeds are rich in oil, about 60% of its content, being a potential source for biodiesel production [77]. However, a production system is not yet developed.

The macaúba (*Acrocomia* spp.), sometimes called Macaw palm, reaches 10–15 m. Different species of this palm tree are found throughout South America. In Brazil, macaúba is found in the states of Pará, Mato Grosso do Sul, Rio de Janeiro and São Paulo. The fruits present a yellow-greenish color; its pulp is used in culinary applications. The seed has high amount of high-quality oil: 20–30% oil content, rich in of lauric acid, which accounts for 45% of its oil content [78].

Licuri (*Syagrus coronata*), also known as ouricuri, is a palm tree with 8–11 m. The licuri plant produces up to 8 clusters with about 1357 fruits 1.4 cm in diameter [78]. This palm tree is found in the states of Minas Gerais, Bahia, Pernambuco, Sergipe and Alagoas. The licuri palm tree seed has 49% of oil content and the palm produces fruits year round [79]. Hitherto, there are few studies about the cultivation of this palm tree.

Buriti (*Mauritia flexuosa*), also known as muriti, is a palm tree found in Amazonian region. This palm tree reaches 20–25 m, with several branches supporting the fruits. The elliptical fruits are 4–7 cm long. The pulp of its fruits has 19% oil content, predominantly oleic acid [80].

5. Future prospects

Since PNPB was launched, Brazil has become one of the world's top biodiesel producers (Fig. 1). This has enabled Brazil to anticipate in 3 years the mandatory biodiesel blend of 5% (B5). Biodiesel production in Brazil has increased over the years (Fig. 2b) and it is expected that this trend will continue because of the increase in biodiesel demand due to mandatory blends. However, its production is still not cost efficient [81].

The Brazilian biodiesel industry is using only 47% of its capacity (Fig. 2) [17]. The region with largest biodiesel production and nominal capacity is the Center-west followed by the South. Although the Southeast region of Brazil is where the largest urban centers and biodiesel consumers are located, this region's biodiesel industry has a small nominal capacity (NC). Over the next decade, a decrease of 1% per year in the participation of soybean as a feedstock for biodiesel production is expected, corresponding to a 70% decrease by 2020 [17]. Nevertheless, because of Brazil's tradition in producing soybeans, the well-established production chain and the use of the soybean bran as cattle feed, soybean oil will most likely remain as an important biodiesel feedstock. However, in the future, Brazil can improve the economics of the soybean agribusiness by extracting the less valuable oil to produce biodiesel and export the bran as animal feed instead of exporting whole grain [17].

On the other hand, it is expected that seeds with higher oil yield than soybeans will increase their participation as feedstocks for biodiesel production. As discussed previously, it is difficult to compare different crops and many factors can contribute to the best regional alternative. Therefore, a diversification of the oil crops used for biodiesel production in Brazil is desirable. Research leading to improved crop varieties, domestication of more exotic species, information about pathogens and optimization of crop management practices will likely play a significant role as to which oil crops will become important biodiesel feedstocks in the future. Ideally, each region of the country will plant its own feedstock and produce biodiesel from it in local industrial plants.

Today Brazil is an important producer and consumer of biodiesel. It also has a tradition in producing ethanol from sugarcane sucrose. The size of the Brazil's bioethanol and biodiesel industries alone, make it a world power in sustainable biofuel production. The ability to produce affordable biomass in large quantities and Brazil's large unused industrial capacity for biodiesel production make it likely that it will continue to play an important role in this sector. Companies that use new technologies such as synthetic biology that allow the conversion of sucrose into hydrocarbon molecules including a renewable diesel are taking a special interest in Brazil. In this scenario, Brazil may be an early adopter of green technologies at industrial scale.

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